

Silver Polyhedron Coated Electrospun Nylon 6 Nano-Fibrous Membrane with Good Infrared Extinction, Ultraviolet Shielding and Water Vapor Permeability

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Received 31 May 2010; accepted 7 September 2010

DOI 10.1002/app.33472

Published online 13 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Silver polyhedron coated electrospun nylon 6 nanofibrous membranes were produced using a nonhazardous and “green” electroless process. The process employed sodium citrate as a complexing and reducing agent at 80°C, without the need of any surfactant or hazardous chemicals. The novel nanofibrous membrane, produced under optimum conditions, demonstrated high infrared (IR) extinction and ultraviolet (UV)

blocking and good water vapor permeability. It is expected to have wide potential application for thermal radiation shielding, UV blocking and IR camouflage. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5138–5144, 2012

Key words: coatings; fibers; thin films; nanotechnology; thermal properties

INTRODUCTION

Fibrous materials, especially nano-fibers, have large surface areas. Coating such materials with metal or metal oxide can impact exceptional properties, such as catalysis, radiation shielding and antimicrobial.^{1–4} In particular, silver is a popular coating material because of its diverse applications, such as enhanced surface Raman scattering (SERS), antibacterial, and catalysis.^{1,5–7} Recently, researchers have become interested in coating silver nano-particles onto nano-wires or nano-fibers and thereby imparting additional beneficial properties. For example, Fang et al.⁸ produced silver coated Si nano-wires with a significantly enhanced SERS effect using the Si on the surface of nano-wires as reducing agent after the removal of surface silicon oxide by means of hydrogen fluoride (HF). The disadvantage of this process is that it uses HF which is hazardous.

Infrared (IR) shielding is very important for masking the IR signature or view-ability of an object or person in order to evade detection, shielding against thermal radiative heat loss being involved as people and equipment emit IR radiation.⁹

This article reports on the development of a non-hazardous and green electroless process for coating silver polyhedrons compactly and continuously onto an electrospun nylon 6 nano-fibrous membrane, employing sodium citrate as complexing and reducing agent. The aim was to produce a novel material having good IR and ultraviolet (UV) shielding properties for potential use as covers for equipment or in clothing for IR camouflage and for thermal insulation by reducing radiative heat loss.

EXPERIMENTAL

Electro-spinning nylon 6 nano-fibrous membrane

A nylon 6 solution of formic acid (25 wt %) was prepared by dissolving 5 g nylon 6 powder (AR) in 15 g formic acid (AR) at room temperature, and continuously “magnetic” stirring for at least 12 h until a transparent solution was achieved. Then the solution was inserted into a 20 mL plastic syringe with a stainless steel nozzle of 0.4 mm in diameter. For electrospinning, the distance between the cathode and anode was fixed at 15 cm and an electric voltage of ~ 15 kV was applied between the nozzle and the collecting electrode which was covered with aluminium foil. The typical ejection rate of the solution from the syringe was 3 $\mu\text{L}/\text{min}$. Electro-spinning occurred in air for 24 h. The resulting nylon 6 nanofibrous membrane was peeled off from the aluminium foil and cut into squares which were fixed on a plastic frame using elastic bands prior to coating with silver polyhedrons.

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Contract grant sponsor: Research Grant Council of HKSAR (GRF Project); contract grant number: PolyU 5162/08E.

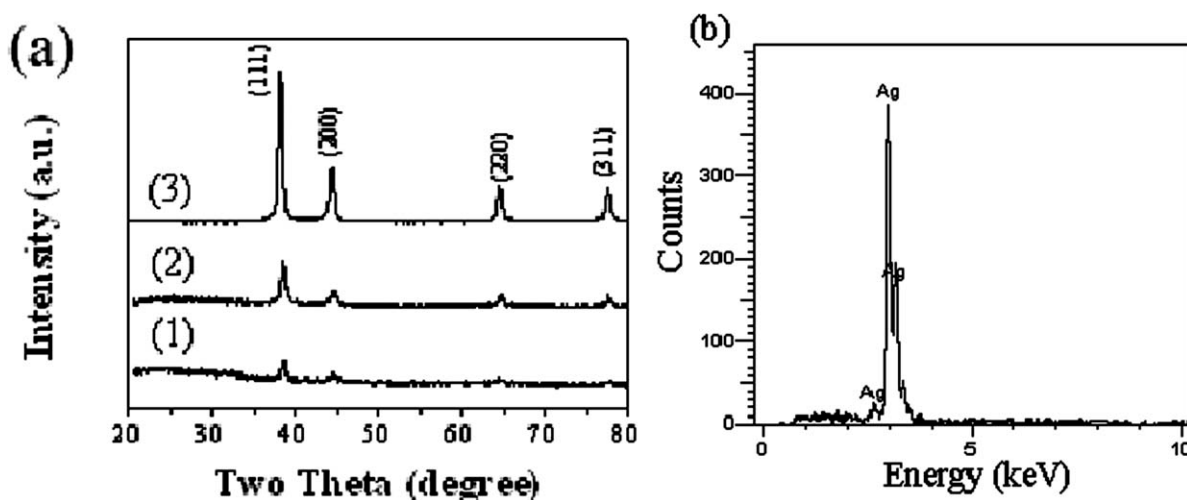


Figure 1 (a) XRD patterns of the electrospun nylon 6 nano-fibrous membrane after silver coating for different times; (1) 0.5 h; (2) 1 h; (3) 1.5 h. (b) EDS spectrum of the electrospun nylon 6 nano-fibrous membrane silver coated for 1.5 h.

Coating Silver polyhedrons onto nano-fibrous membranes

At first, the electrospun nylon 6 nano-fibrous membranes were dipped in sensitising (stannous chloride (AR) 4 g/L; hydrochloric acid (AR, 37%) 4 mL/L) and activation (palladium chloride (AR) 0.4 g/L; hydrochloric acid (AR, 37%) 6 mL/L) solutions for 5 min, respectively, at room temperature. After this, the membranes were washed three times in de-ionized water. In the silver (Ag) coating (plating) process, the membrane was placed in the electroless solution (silver nitrate AR 0.02 M; sodium citrate AR 0.08 M) at room temperature. Thereafter, the electroless solution was heated to 80°C and kept at that temperature to produce coating times of 0.5 h, 1.0 h, and 1.5 h, respectively, with 1.5 h taken as the “typical” time. The sample was removed when the coating was complete. The sample was rinsed three times in de-ionized water and ethanol, respectively. Finally, the sample was dried in a vacuum oven at 60°C for 2 h.

Characterisation

The X-ray diffraction (XRD) patterns of the samples were recorded by means of a Philips Xpert XRD System with Cu K α radiation at a scanning rate of 0.02° S⁻¹ in a 2 θ range of 20–80°. Scanning electron microscopy (SEM) images were obtained on a FEI Sirion 200 field emission SEM, with energy-dispersive X-ray spectroscopy (EDS) attached. High-resolution transmission electron microscope (HRTEM) images were obtained on a JEM-2010FEF. The thickness of the membrane was measured on a MITU-TOYO LITEMRTIC VL-50R.

IR extinction of the material was measured by means of a Nicolet Magna 760 Fourier transform

infrared (FTIR) spectroscopy. The UV absorption spectrum was obtained by means of a Lambda 18 UV-vis spectrometer. Water vapor transmission rate (WVTR) was measured under standard atmospheric conditions of 22°C and 65% relative humidity according to the British Standard BS7209 (1990) water vapour transmission dish method. The total amount of water vapor transferred through the membrane from the water dish within a 24 h period was determined. The bending length of the membrane was measured by a fixed-angle (41.5°) flexometer according to the British Standard BS3356 (1990).

RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns of the silver coating for different coating times, all other conditions being the same. The different diffraction peaks could be indexed to the (111), (200), (220), and (311) planes, respectively, of the face-centered cubic (fcc) silver crystal (JCPDS No. 4-783). No peaks of impurities could be detected from the XRD patterns, which indicated that a pure silver coating was obtained under the present coating conditions. The intensity of all the diffraction peaks increased with increasing coating time, which indicated the degree of crystallization of the silver could be increased by increasing the coating time. The EDS spectrum of the silver coating is shown in Figure 1(b). Analysis of the spectrum also indicated that the coating consisted of silver only.

Figure 2(a) is an SEM image of the uncoated membrane, which indicates that the diameter of the nylon 6 nano-fibers is about 400 nm, the fibers being randomly arranged. The inset in Figure 2(a) shows that the surfaces of the as-spun fibers are smooth. Figure 2(b, c) are SEM images of the as-prepared silver

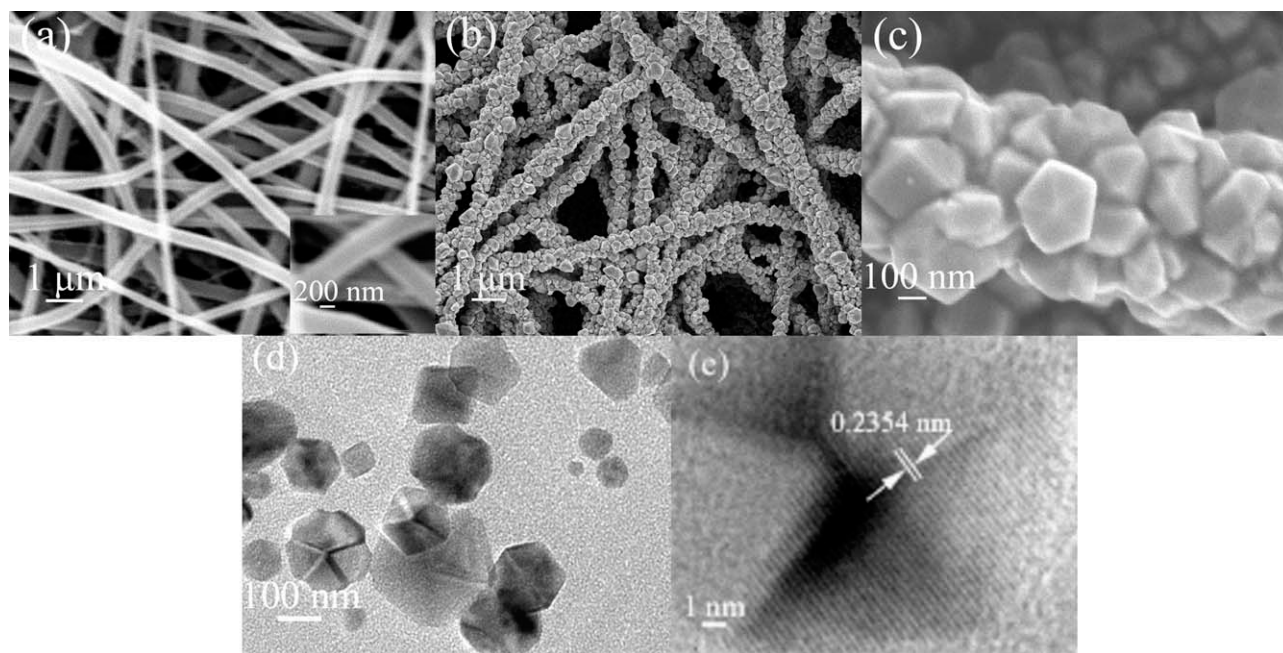


Figure 2 (a) Low-magnification SEM image of the uncoated electrospun nylon 6 nano-fibrous membrane: The inset shows the high-magnification SEM image; (b and c) SEM images of the coated electrospun nylon 6 nano-fibrous membrane silver coated under typical conditions; (d) TEM image of the silver crystals; (e) HRTEM image of a silver polyhedron.

coated membrane. From these two SEM images, it can clearly be seen that the outer surfaces of the coated nano-fibers were rough and covered by a dense silver layer, with the coating layer increasing the diameter of the fibers to about 500–700 nm. Figure 2(b) shows that the porous structure of the nano-fibrous membrane was not changed, while Figure 2(c) shows that the coating consisted of silver polyhedrons, some small silver nano-particles sometimes being attached to the plane of the silver polyhedron [Fig. 2(c)], indicating that the silver polyhedrons might be formed by the adsorption of small silver nanoparticles via an Ostwald ripening mechanism.¹⁰ Du et al.¹¹ also believed that, during the reaction process, new nuclei could be continually produced, which adhered to the edges of the larger particles because of diffusion. The TEM image [Fig. 2(d)] of the silver crystals formed in the same solution also shows that the structure of the silver crystals was polyhedron. The HRTEM image [Fig. 2(e)] indicates that the lattice distance was 0.2354 nm, which was nearly the same as the {111} lattice distance (0.2359 nm) of the face-centered cubic (fcc) silver crystal (JCPDS no. 4-783).

The time-dependent experiments were carried out for coating times of 0.5 h and 1.0 h, all other conditions being the same. When the coating time was 0.5 h [Fig. 3(a, b)] the silver coating comprised of smaller nano-particles and the coating was not continuous. When the coating time was increased to 1.0 h, the silver coating comprised of nano-particles

and some polyhedrons [Fig. 3(c, d)], with the particle density and continuity of the silver coating increased. Based on these results, it can be reasonably concluded that the silver polyhedrons were formed from the nano-particles via the Ostwald ripening mechanism.

The process of crystal growth can be divided into an initial nucleating stage and a subsequent crystal growth stage. The crystalline phase during nucleation and also the growth rate difference between the surfaces of the crystal determine the overall nano-structure.¹² Surface energies associated with different crystallographic planes are usually different. A general sequence may be $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$ for an fcc crystal.¹³ The crystal surfaces with low free energies are easier to expose in large proportions,¹⁴ because the lower energy surfaces grow at slower speeds than the higher energy surfaces.

Palladium nuclei (seeds) have been used as catalyst in plastic electroless processes, initiating the reaction and enhancing the adhesion of the coating due to the existence of crystal nuclei.^{15,16} Before coating, the nylon 6 fibers should be sensitized and activated so as to generate palladium nuclei (seeds) on the surface. The existence of easily oxidized Sn^{2+} is favourable for the formation of an activation layer in the next process, which could initiate the reaction and enhance the adhesion of the coating due to the existence of crystal nuclei.¹⁵ When the experiment was carried out without palladium nuclei (seeds) [Fig. 3(e, f)], discontinuous layer of silver nano-

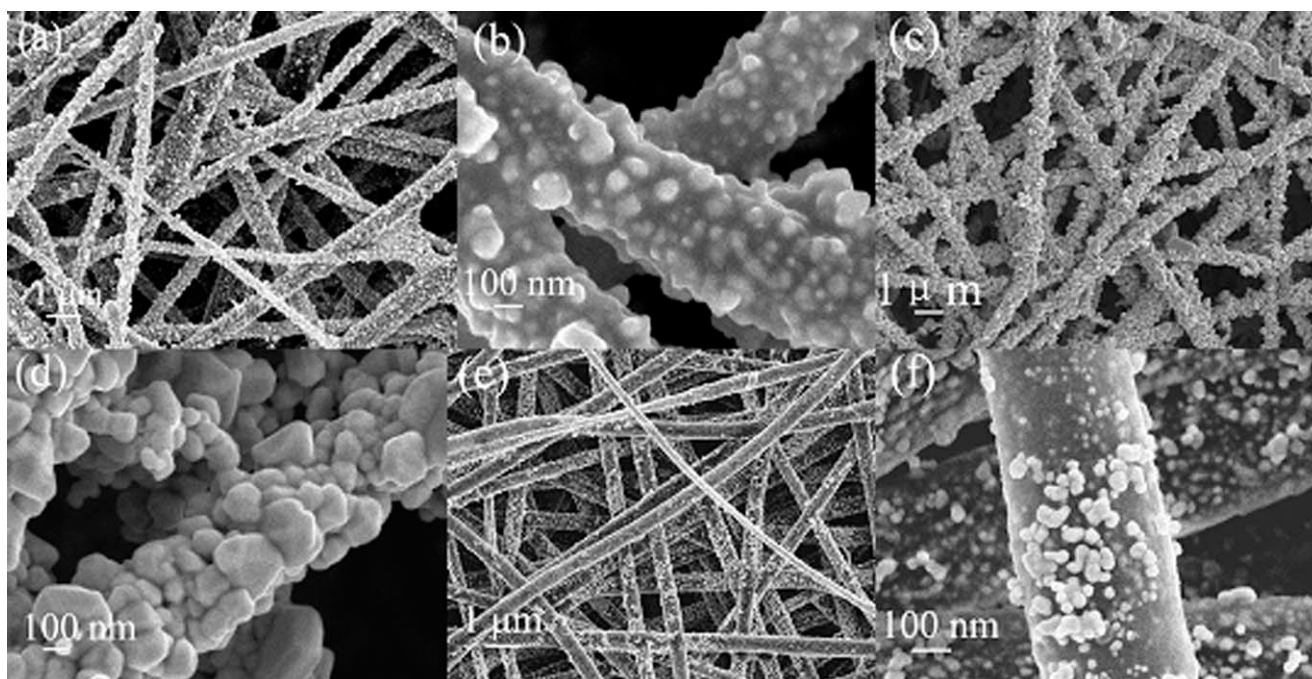


Figure 3 (a–d) SEM images of the electrospun nylon 6 nano-fibrous membranes, silver coated for different times; (a and b) coated for 0.5 h; (c and d) coated for 1.0 h; (e and f) SEM images of the electrospun nylon 6 nano-fibrous membrane silver coated without palladium (Pd) seeds (nuclei).

particles was coated on the fibers, which indicated that the existence of palladium seeds not only favored the formation of a continuous dense coating on the fibers but also affected the geometrical structure of the silver coating.

Based on the above experiments and analysis, the process of forming the polyhedron silver coating can be predicted and is shown in Figure 4. At first, Sn^{2+} was adsorbed on the electro-spun nylon 6 fiber in the sensitization solution. Second, PdCl_4^{2-} was adsorbed on the nylon 6 fiber and reduced rapidly by Sn^{2+} to form palladium (Pd) nuclei on the electrospun nylon 6 fiber in the activation solution. Then silver nano-particles were formed using the palladium as crystal nuclei.^{15,16} The $-\text{COO}^-$ and $-\text{OH}$ groups of citrate could complex Ag^+ to form silver-

citrate complexes in the electroless solution, the silver-citrate complex being adsorbed on the nylon 6 fibers. The nuclei then grew through an Ostwald ripening process when the silver-citrate was reduced by the citrate in situ. The different crystal planes of face-centered cubic silver crystals have different surface energies.^{12,13} The lower energy plane of the silver crystal was mainly exposed due to the slow growing speed associated with the citrate. Finally, the silver coating, comprising of polyhedrons, was formed through an Ostwald ripening process.

Previous studies have shown that radiative heat transfer can be a significant contribution to the total heat transfer within porous media.^{17,18} Introducing a thin polymer film with a relatively high IR extinction, as an interlayer within a highly porous media,

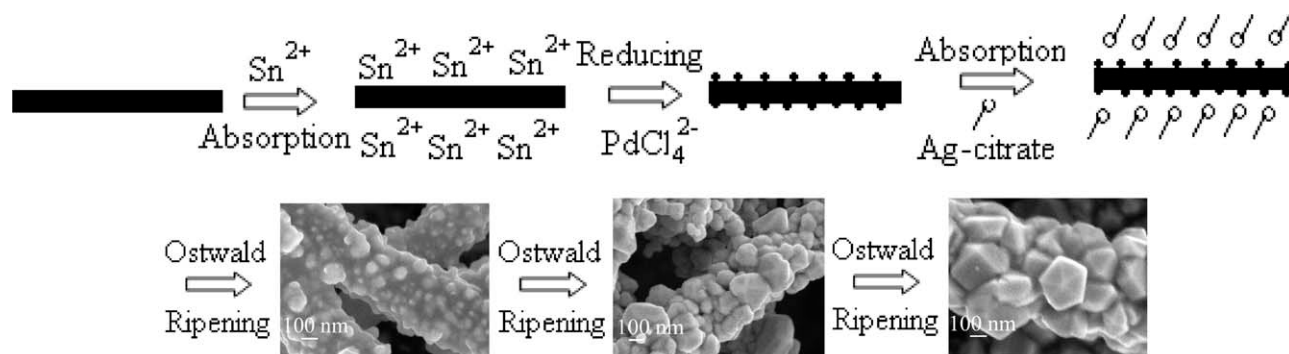


Figure 4 The sequential steps in the silver polyhedron coating process.

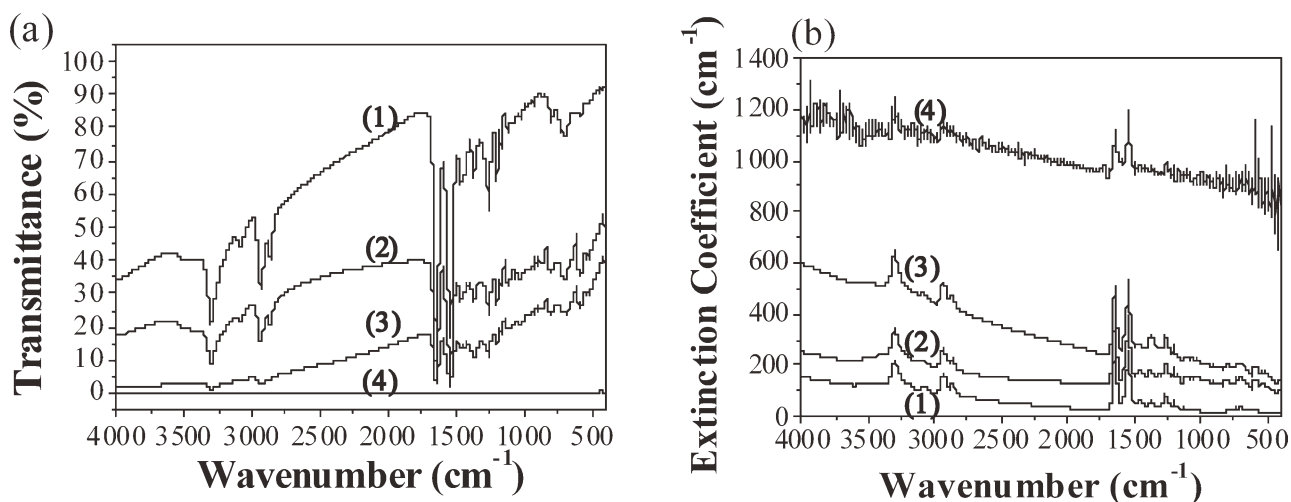


Figure 5 (a) IR transmittance and (b) $\sigma_{e,\lambda}$ extinction coefficient (b) spectra of uncoated and silver coated nylon 6 nanofibrous membranes coated for different times. (1) The uncoated membrane; (2) 0.5 h coating time; (3) 1.0 h coating time; (4) 1.5 h coating time.

is a promising way of blocking radiation, and reducing the total heat flow. Therefore, evaluating the radiative thermal properties of thin polymer films is essential when attempting to improve the thermal insulating performance of assemblies. FTIR has been applied to evaluate the thermal radiative properties of foams as well as those of thin polymer films and superfine electrospun PVA membranes.^{19–22}

Figure 5(a) compares the IR transmittance spectra of the four different electrospun nylon 6 fibrous membranes and shows that the IR transmittance was significantly reduced after the fibrous membrane was coated with the silver crystals. The IR transmittance was further reduced when the coating time was increased, being almost zero with a coating time 1.5 h [Fig. 5(a) (4)]. The number and dimensions of the silver crystals were increased when the coating time was increased (Fig. 3). It therefore seems logical to conclude that increasing the quantity and dimensions of the silver crystals decreased the IR transmittance. IR reflectance can be increased by increasing the carrier concentration and carrier mobility.²³ The IR transmittance was decreased due to the increase in free carrier mobility after coating with silver. It is also reasonable to expect that increasing the amount of conducting silver should also increase the electron mobility due to the reduction of the interface effects as the coating layer becomes thicker, thereby leading to higher IR reflectance.

The transmittance percentage (τ_λ) is the ratio (expressed as a percentage) of the radiation intensity transmitted through the sample [$I_{\lambda(\lambda)}$] to that incident to the sample [$I_{0,\lambda}$].

$$\tau_\lambda = I_{\lambda(\lambda)}/I_{0,\lambda} \quad (1)$$

According to Beer's law,^{19,24} the spectral extinction coefficient of IR for a thin film ($\sigma_{e,\lambda}$) can be obtained from the transmittance spectrum (τ_λ) and the thickness of the film (L) as follows:

$$\sigma_{e,\lambda} = -\ln(\tau_\lambda)/L \quad (2)$$

The thickness of the nano-fibrous membranes used in all the coating processes was 0.0702 mm. The thicknesses of these membranes coated with silver for 0.5 h, 1.0 h, and 1.5 h, respectively, were 0.0707, 0.0716, and 0.0719 mm, respectively, increasing only very slightly with increasing coating time.

As can be seen from Figure 5(b) the spectral extinction coefficients ($\sigma_{e,\lambda}$) of the samples increased noticeably after the fibrous membrane was coated with silver, also increasing with an increase in the coating time. The results show that silver coating increases the IR extinction. IR reflectance can be increased by increasing the carrier concentration and carrier mobility of the silver coating.²³ Based on the past literature, the increase of IR extinction is most likely caused by the increasing of IR reflection.^{25–27}

To quantitatively compare the extinction coefficients, an apparent Rosseland mean extinction coefficient ($\sigma_{e,R}$) was introduced, it being determined using the Rosseland approximation:²⁰

$$\frac{1}{\sigma_{e,R}} = \int_0^\infty \frac{1}{\sigma_{e,\lambda}} \frac{\partial e_{b,\lambda}}{\partial e_b} d\lambda \quad (3)$$

where $e_{b,\lambda}$ is the spectral black body emissive power, e_b is the black body emissive power, and λ is the wavelength.

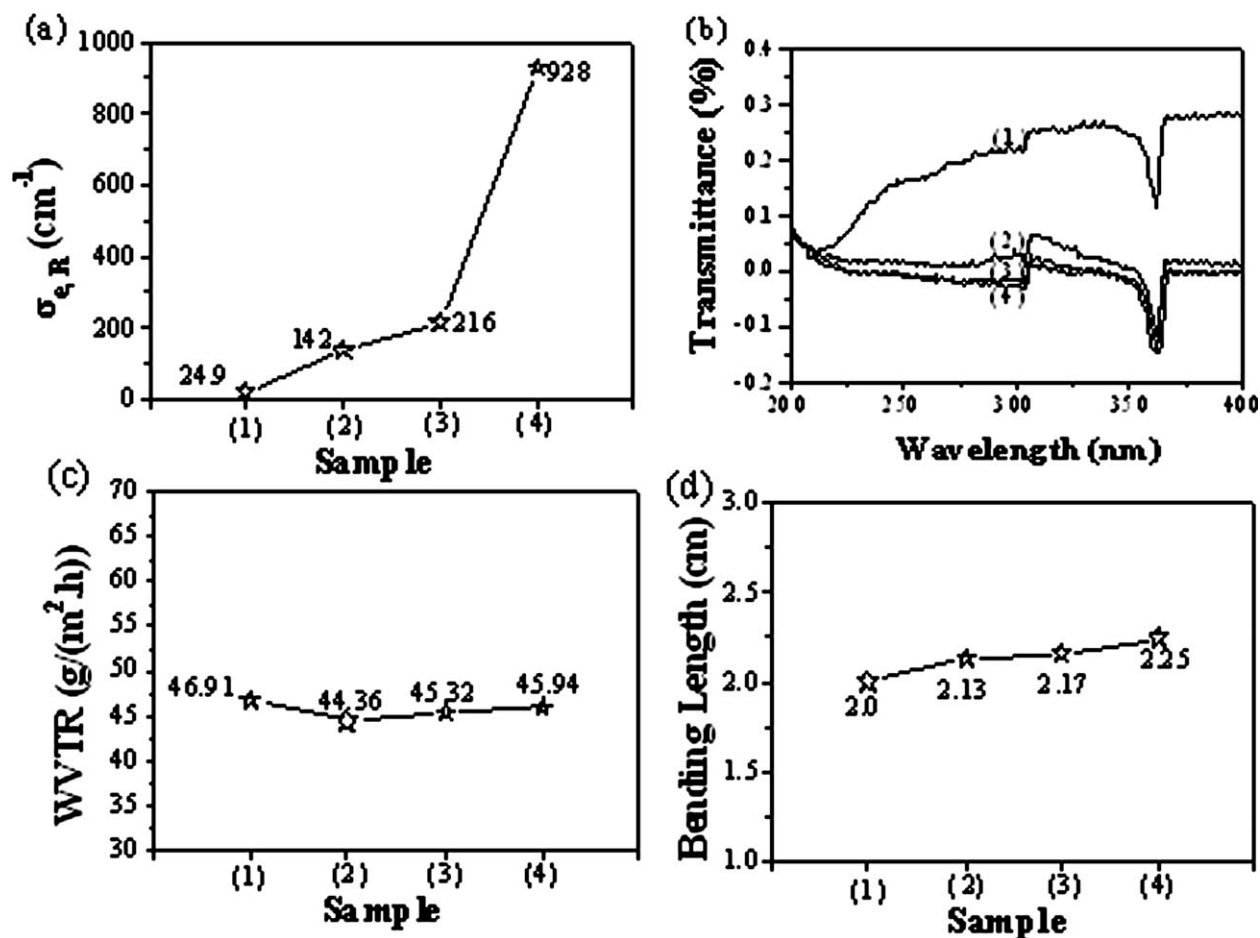


Figure 6 The $\sigma_{e,R}$, UV, WVTR and bending length results of the various electrospun nylon 6 nano-fibrous membranes; (a) $\sigma_{e,R}$; (b) UV spectra; (c) WVTR; (d) bending length. (1) Uncoated membrane; (2) 0.5 h coating time; (3) 1.0 h coating time; (4) 1.5 h coating time.

The results of $\sigma_{e,R}$ for these samples [Fig. 6(a)] show that $\sigma_{e,R}$ is increased significantly, from 24.9 (cm^{-1}) to 142 (cm^{-1}), after coating the nano-fibrous membrane with silver for 0.5 h, indicating that silver coating such a membrane might provide an effective method to improve the thermal radiation extinction of insulation systems. The $\sigma_{e,R}$ was increased further to 928 (cm^{-1}), when the coating time was increased to 1.5 h, indicating that better extinction coefficients can be obtained through the optimization of the coating time.

Figure 6(b) illustrates the UV transmittance spectra of the four different nano-fibrous membranes, from which it is apparent that the UV transmittance was substantially decreased by the silver coating, the decrease in transmittance being slightly greater for the longer coating times. The silver coated nano-fibrous membrane can therefore also be used for UV shielding.

The WVTR of the various coated and uncoated membranes is shown in Figure 6(c), from which it can be seen that coating with silver hardly changed the WVTR. This behavior was expected since the silver coating was deposited directly onto the nano-

fiber without affecting the porous structure of the membrane system. In view of the significant improvement in thermal radiation extinction with little adverse effect on water vapor transmission, the novel silver coated nylon 6 nano-fibrous membranes can be expected to find wide application in high-performance, thermal resistant and moisture-permeable systems for extremely cold environments.

For evaluating the flexibility of these membranes, the bending lengths of the membranes were measured. Figure 6(d) shows that the bending length of the membrane increased a little after the membrane was coated with silver, which indicates that the flexibility of the membrane was slightly decreased after coated silver.

CONCLUSIONS

A new nonhazardous and eco-friendly method for producing silver coated electrospun nylon 6 nano-fibrous membranes was developed, the silver polyhedron coating being formed from nano-particles

through an Ostwald ripening process. When the processing conditions were optimized, the silver coated nano-fibrous membrane showed exceptionally high IR and UV extinction, with hardly any effect on the water vapor transmission rate. The novel silver coated nano-fibrous membrane should find application in high-performance, thermal resistant and moisture-permeable civil and military or paramilitary systems, where thermal insulation, IR camouflage and UV blocking are important requirements.

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